



PCT/AU2004/001523

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PROVISIONAL SPECIFICATION

for the invention entitled:

"Metal Oxide Materials

The invention is described in the following statement:

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METAL OXIDE MATERIALS

Field of the Invention

5 The present invention relates generally to metal oxide material having co-continuous architecture. More particularly, the present invention is directed to a metal oxide or a composite metal oxide material having a surface which has been modified to have co-continuous architecture. The co-continuous architecture of the metal oxide or composite material permits or otherwise facilitates accessibility of the surface of the material to an
10 external environment. The accessible, i.e. co-continuous, nature of the surface of the materials of the invention allows the materials to be used in applications where high surface area metal oxide materials are required. The processes for generating such high surface areas in the materials of the present invention also generally provides useful mesoporosity characteristics which make them useful in various applications where
15 mesoporous metal oxide materials are required. The metal oxide materials of the present invention may be used as catalysts, for example in the removal of SO₂, NO and HCl, in energy storage, for example in the production of supercapacitors, in water treatment, for example in water filtration to remove organics, bacteria, viruses, heavy metals and other contaminants, in separation processes, such as the removal of metal ions from solutions, or
20 as templates for metal oxide nanoparticle preparation. The present invention further provides processes for generating these metal oxide and composite metal oxide materials, and their use in applications such as those referred to above.

Background of the Invention

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Reference to any prior art in the specification is not, and should not be taken as, an acknowledgment or any form of suggestion that this prior art forms part of the common general knowledge in Australia or in any other country.

30 Bibliographic details of the publications referred to in this specification are collected at the end of the description.

Various methods have been described in the prior art for making and using these materials, however these processes are limited in relation to the surface area per weight of material
10 which can be achieved.

The production of composite activated carbon/iron oxide materials having magnetic properties for use in the treatment of water has been described by Oliviera, Luiz C. A.; Rios, Rachel V. R. A.; Fabris, Jose D.; Garg, V.; Sapag, Karam; Lago, Rochel M. *Carbon* 40:2177-2183, 2002. This process involved the suspension of activated carbon in a solution of FeCl_3 and FeSO_4 at elevated temperature followed by treatment with a large excess (> 4 to 5 times the stoichiometric ratio need to give a neutral solution) of sodium hydroxide to precipitate the magnetic ion oxides, magnetite and maghemite. These oxides were then obtained and dried in an oven to produce composite materials having surface areas, as determined by BET, of $658 \text{ m}^2/\text{g}$. When the iron oxide material was prepared in the absence of the activated carbon the surface area obtained was only $66 \text{ m}^2/\text{g}$.

Perez-Maqueda, Luis A.; Criado, Jose Manuel; Real, Concepcion; Balck, Vladimir; Subrt, Jan. *Journal of the European Ceramic Society*, 22:2277-2281 (2002) describe the preparation of porous hematite by subjecting goethite to thermal decomposition using constant rate thermal analysis equipment. The porous hematite product had a low surface area, with 85 m²/g being the maximum achieved.

30 Schwickardi, Manfred; Jaohann, Thorsten; Schmidt, Wolfgang; Schuth, Ferdi, *Chem. Mater.* 14:3913-3919 (2002) describe the preparation of high surface area oxides using activated carbon. These materials were prepared by combining activated carbon with

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metal nitrates and subjecting the mixture to calcination at high temperature for a short period of time. When using $\text{Fe}(\text{NO}_3)_3$ the calcination was performed at 450°C for 1 hour. The best surface area which could be achieved for this material via this route was $123 \text{ m}^2/\text{g}$.

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Tseng, Hui-Hsin; Wey, Ming-Yen, Liang, Yu-Shen; Chen, Ke-Hao, *Carbon* 41:1079-1085 (2003) describe the catalytic removal of SO_2 , NO and HCl from incineration flue gas using activated carbon-supported metal oxides. These materials were prepared by impregnating pre-treated activated carbon material with aqueous solutions of nitrite salts followed by stirring and heating to remove most of the liquid. The impregnated activated carbon was then dried followed by calcination at high temperature (500°C) for 4 hours. For Fe_2O_3 the best surface area achieved for the composite material was $897 \text{ m}^2/\text{g}$. The material also had a low mesoporous volume of $0.0503 \text{ cm}^3/\text{g}$.

15 Ching-Chen Hung (U.S. Patent Nos. 5,948,475 and 5,876,687) describes processes for preparing various metal oxide, metal and composite materials which involve the exposure of graphite oxide to a metal chloride to form an intermediate carbonaceous product comprising elements of metal, oxygen and chlorine. This product is then treated to remove the chlorine and/or the carbon. This latter treatment involves heating to temperatures of 20 250°C and above. It is clear from the data presented in the specification that the surface areas achieved utilising these processes were very low.

Oh *et al.* in WO01/89991 describe the preparation of mesoporous carbon material, carbon/metal oxide composite materials and electrochemical capacitors prepared from 25 them. No surface area data is provided for the metal oxide containing materials.

In the present invention new metal oxide and metal oxide composite materials have been identified which have high surface areas and/or high mesoporous areas, making them particularly useful in a number of important applications. Methods of generating these materials have also been identified which may be performed using inexpensive materials 30 and relatively low temperatures compared to the prior art processes. These processes may

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be used to produce metal oxides and metal oxide composite materials having more surface area continuous with the external environment than prior art materials. Such a state is referred to herein as "co-continuous".

5 Summary of the Invention

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps
10 but not the exclusion of any other integer or step or group of integers or steps.

The present invention relates generally to the generation of metal oxide and composite metal oxide material with co-continuous architecture and other properties. In particular, the present invention provides metal oxides and composite metal oxide materials having
15 co-continuous architecture, where "co-continuous" means that the accessibility of the surface of the material to an external environment is facilitated. This co-continuity can generally be achieved through a multiplicity of pores or porous-like structures. The pores or porous-like structures may exist singly or each porous region may comprise multiple pores or porous-like structures, resulting in a potentially high extensive surface which is
20 co-continuous with the external environment.

The accessibility of the surface to the external environment (i.e. co-continuity) facilitates contact with the materials during chemical and electrochemical processes and in separation and adsorption applications.

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Accordingly, the present invention provides a metal oxide or composite metal oxide material comprising a surface modified to facilitate co-continuity to an external environment.

30 The metal oxide may be a single metal oxide or a mixture of metal oxides, or the material may be a composite material comprising metal oxides or mixtures thereof in combination

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with a substrate material. This substrate material may be a substrate having a surface modified to facilitate co-continuity to an external environment. Examples of such substrate materials include activated carbon, mesoporous silica, metals, structured or unstructured synthetic polymer materials, natural biopolymer materials, polymer/inorganic hybrid materials, other two phase systems, such as emulsions and gels, self assembled structures, such as surfactant lyotropic mesophases, weaved materials, such as porous fabrics and fibres, carbon nanotubes and other high aspect ratio materials, synthetic polymer foam and inorganic foams, and biologically deposited organic and inorganic structures, such as diatom skeletal materials.

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Accordingly the present invention provides a composite metal oxide material comprising a substrate with a surface modified to facilitate co-continuity to an external environment and a metal oxide material attached to, bound within or otherwise associated with said substrate such that the composite material maintains co-continuity to an external environment.

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In a preferred method the metal oxide material is prepared by treating a metal salt with a base to precipitate metal hydroxide or metal oxide followed by solvent removal under conditions that convert any metal hydroxide to metal oxide. Following solvent removal the solid residue is then treated to remove any residual salt.

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Accordingly the present invention provides a process for generating a metal oxide material with a surface modified to facilitate co-continuity to an external environment comprising treating a metal salt with a base in an aqueous medium for a time and under conditions sufficient to precipitate metal hydroxide and/or metal oxide in said aqueous medium, removing water from the aqueous medium by evaporation, under conditions that convert any metal hydroxide to metal oxide, to provide a solid residue, and removing salt from the solid residue to thereby generate said metal oxide material with surface modified to facilitate co-continuity to an external environment.

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The present invention further contemplates the performance of this process in the presence

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of a substrate with a surface modified to facilitate co-continuity to an external environment. Such a substrate may be a metal oxide or composite metal oxide material prepared according to the invention, or may be a mesoporous substrate, such as activated carbon or mesoporous silica or the like as described above.

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Accordingly the present invention provides a process for generating a composite metal oxide material with a surface modified to facilitate co-continuity to an external environment comprising treating a metal salt with a base in an aqueous medium in the presence of a substrate with a surface modified to facilitate co-continuity to an external
10 environment for a time and under conditions sufficient to precipitate metal hydroxide and/or metal oxide, removing water from the aqueous medium by evaporation, under conditions that convert any metal hydroxide to metal oxide, to provide a solid residue of metal oxide attached to, bound within or otherwise associated with said substrate, and removing salt from the solid residue to thereby generate said composite metal oxide
15 material with surface modified to facility co-continuity to an external environment.

Detailed Description of the Preferred Embodiments

The present invention is predicated in part on the generation of metal oxide and composite
20 metal oxide materials with co-continuous architecture and other properties. These materials have extensive surface regions freely accessible, i.e. co-continuous, to the external environment.

Reference to the "external environment" in this context includes a surrounding solvent,
25 solution or other liquid, gel, vacuum or gaseous environment comprising, for example, entities capable of reacting or interacting or binding with the surface of the material, or accepting or donating electrons from and to the surface of the material.

A solvent is any liquid phase in which reactants are dissolved, suspended or dispersed in
30 the liquid medium. Solvents include, but are not limited to, polar or non-polar, protic or aprotic solvents such as hydrocarbons (e.g. petroleum ethers, benzene, toluene, hexane,

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cyclohexane), chlorinated solvents (e.g. dichloromethane, carbon tetrachloride) and other halogenated solvents including fluorinated or brominated solvents, dialkyl ethers (e.g. diethylether, tetrahydrofuran), alcohols (e.g. methanol, ethanol, propanol and butanol), acetonitrile, ethylacetate and aqueous media, including buffer solutions or water alone.

- 5 The solvent may also be a solvent mixture.

- The external environment may also include other liquid environments, such as raw water, for example, from a river, reservoir or the like, industrial waste water, hospital waste water, domestic waste water or industrial process water. The liquid may also be other
- 10 liquid materials that have been utilised in industrial processes. The liquid material (or gel) could also be an electrolyte solution used in an electrolysis cell, battery, capacitor or the like.

- The external environment may also be a gaseous environment, such as an inert gas, for
- 15 example, a nitrogen atmosphere or air, exhaust gas, combustion engine or industrial process gas, vapours, or the like, biologically generated gases from industrial fermentation processes or sewage or exhaled/emitted from plants and animals, such as CO₂, methane etc.

- 20 The metal oxides and metal oxide composite materials according to the present invention may be in the form of spheres, rods, sheets, blocks, fibres, discs, capsules, networks, weaves or biologically deposited complex structures, such as diatom skeletal materials. The shape of the material may be dictated by the apparatus used to manufacture the material, or the generated materials may be subjected to treatments which alter or refine
- 25 shape following generation. The shape of the material may be dictated by the shape of the substrate material used in the case of the composite metal oxide materials. Particularly preferred shapes are those that enhance the activity of the material for its intended purpose.

- The metal salts which are hydrolysed with base to produce the metal hydroxides/oxides
- 30 may be any water soluble metal salt that is capable of being converted to an insoluble hydroxide/oxide by treatment with base. Depending on the nature of the oxide material

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desired, mixtures of salts may be used, including mixtures of salts of different metals. This may produce mixed metal oxide materials. Examples of suitable metal salts include the halides (e.g. chlorides, fluorides, bromides and iodides), acetyl acetates, sulphides, sulphates, nitrates, nitrides, cyanides, carbides, silanes, alkoxysilanes, and acetates of transition metal elements such as titanium, zirconium, vanadium, niobium, tantalum, chromium molybdenum, tungsten, manganese, iron, cobalt, iridium, lanthanum, nickel, lead, aluminium, silver, gold, copper, zinc, mercury, cadmium, arsenic and ruthenium. other suitable metal salts include those comprising halogen oxoanions (such as bromate and iodate), metal and transition metal oxoanions (such as permanganate, chromate and arsenate) and organic oxoanions, such alkoxides and carboxylates (e.g. ethoxides, acetates and palmitates). Particularly preferred salts are those of Fe^{3+} , such as Fe(III) nitrate, chloride, chlorate, sulphate, perchlorate, nitrite, silicate, borate or phosphate.

The use of mixed or doped materials is also contemplated, where the mixing/doping of additional metals, metal salts, complexes or other chemical species (including biological species e.g. proteins, DNA) confers desirable properties such as fluorescence, electroluminescence, magnetism, semi-conductivity or biological activity on the final material.

Where it is desired to produce a composite metal oxide material the precipitation of the metal hydroxide/oxide may be conducted in the presence of a substrate with a surface modified to facilitate co-continuity to an external environment. Examples of such materials include activated carbon, mesoporous silica or the like as described above, or metal oxide or composite metal oxide materials prepared according to the invention. In order to prepare a suitable composite metal oxide material the metal salt and the substrate may be combined in a suitable ratio in an aqueous medium in the presence of a base. The ratio selected will depend on the nature of the substrate and the amount of metal oxide to be introduced into the composite material. It will also depend on the atomic weight of the metal salt. The metal salt and the substrate will generally be combined in a weight ratio of from 1:100 and 100:1, more preferably from 50:1 to 1:50, more preferably from 10:1 to 1:10. For Fe(III) nitrate a ratio of from 5:1 to 1:1 is preferably advantageous.

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- The metal salt is converted to the metal oxide by increasing the pH of the aqueous solution. This may be done by introducing a suitable base into the aqueous medium. Preferably the base is an inorganic base, such as a strong inorganic base. Examples of suitable strong
- 5 inorganic basis include sodium hydroxide, potassium hydroxide and ammonium hydroxide. While the pH to which the aqueous medium is adjusted will depend on the particular metal hydroxide/oxide the pH is generally adjusted to within a range of 7 to 11, more preferably 7.5 to 8.5.
- 10 The conversion of the metal salt (hydroxide) to the metal oxide generally takes place very quickly at room temperature, although it may be possible to increase the rate by applying heat and by agitating or stirring the aqueous medium. In some cases heat and/or exposure to air is necessary to convert the hydroxide to the oxide. Progress of the conversion can be monitored by testing the medium for the presence of metal salt, or by monitoring the
- 15 formation of the precipitate. The precipitate will generally form as a gel in the aqueous solution. The amount of base is generally chosen such that the final pH of the mixture reaches and stabilises at pH 7.5-8.5. Final pH stability is assumed when the pH no longer changes for a period of about 5 minutes after an addition. Concentrated base (e.g. 6M) can be used in order to maximise the speed of precipitation. Base is preferably added to a
- 20 stirred mixture (e.g. using a magnetic stirrer) dropwise from a pipette at room temperature until the pH is reached, as determined from a pH probe immersed in the stirring mixture. Typically the addition is completed within approximately 15 minutes of initial addition, although the exact time and conditions will depend on the particular metal salts and substrates used.
- 25 After formation of the precipitate/gel of metal hydroxide/oxide in the aqueous medium, the water in the aqueous medium may be removed. While the usual method for recovering a precipitated metal hydroxide/oxide from an aqueous solution would involve a filtration step followed by oven drying, it has been surprisingly found that advantageous
- 30 mesoporosity in the metal oxide or metal oxide containing material can be obtained if the water is removed primarily or totally via evaporation. While not wishing to be limited by

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theory, it is believed that the presence of the salts in the aqueous medium and their concentration through the evaporation process and consequential rise in ionic strength help to retain the network structure in the metal oxide particles upon which further dehydration react to form an interconnected mesoporous material. It is believed that the maintenance
5 of the original gel network structure via control of the surface chemistry (pH, ionic strength) causes the mesoporosity in the metal oxide material, thereby contributing to the co-continuity of the material to an external environment. Evaporation of the water from the aqueous medium can be enhanced by the application of heat. Temperatures of about 100°C and slightly above, for example between 100°C and 110°C, preferably about
10 105°C, are sufficient for this purpose. This heating step can be essential in the case of metal hydroxides which require heat in order to form corresponding oxides.

The conditions during the removal of the water from the aqueous medium should be selected such that the dried residue includes metal oxide or metal oxide containing
15 composite material that, following the removal of residual salt, has a high degree of co-continuity to an external environment. An important measure of co-continuity to an external environment is surface area. In the case of metal oxide materials, including mixed metal oxide materials, the material may have a surface area as measured by BET of greater than 100 m²/g, preferably greater than 200 m²/g, more preferably greater than 250 m²/g. In
20 the case of composite materials involving substrates which already have surfaces modified to facilitate co-continuity to external environments, the final surface area of the material will be in some way dependent upon the surface area of the substrate utilised. However, the surface area of the composite material following metal oxide deposition may be greater than 700 m²/g, preferably greater than 900 m²/g, more preferably greater than 1000 m²/g.

25 The metal oxide or mixed metal oxide materials of the present invention are preferably mesoporous. Mesoporous materials generally have an average pore size of from about 2 to 50 nanometers, although for most applications a pore size of from 2 to 20 or 2 to 10 nanometers is more desirable.

30 The metal oxide and composite metal oxide materials of the present invention may also

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have a high mesoporous area, as measured by BJH. In the case of metal oxide materials, the mesoporous area may be greater than $100 \text{ m}^2/\text{g}$, preferably greater than $150 \text{ m}^2/\text{g}$ and more preferably greater than $200 \text{ m}^2/\text{g}$. For the metal oxide composite materials the mesoporous area as measured by BJH may be greater than $500 \text{ m}^2/\text{g}$, preferably greater than $800 \text{ m}^2/\text{g}$ and most preferably greater than $1000 \text{ m}^2/\text{g}$.

After evaporation of the water and conversion, if necessary, of the hydroxide to the oxide material, it is necessary to remove any residual salt from the metal oxide or composite metal oxide material. This salt is formed during the hydrolysis step when the metal salt is converted to the hydroxide/oxide material. This salt can generally be removed by simple washing of the metal oxide or composite metal oxide material in water. This washing step may be performed by agitating the metal oxide material in a vessel, allowing it to settle and pouring off the water. This washing step may be repeated, after which the material may be dried, for example in a vacuum oven at a suitable temperature, such as 50 to 60°C .

The metal oxide and composite metal oxide materials of the present invention may be used directly as prepared, or may be incorporated into devices or equipment for achieving their intended function. For example, when the materials are to be used as catalysts in the removal of toxic components such as SO_2 , NO and HCl , particles of the materials may be packed into a bed, possibly fluidised, incorporated into a membrane or fibre or filter, possibly in cartridge form, or attached to or supported by another material, e.g. a polymer or inorganic or metallic material. Where the materials are to be used as catalysts for chemical reactions, particles of the material can be simply introduced into the reaction medium, generally a solvent, whereby the material can act as a catalyst for the reaction. Similarly, gas phase reactions may be catalysed by passing the gaseous reactants through a tube packed with appropriate metal oxide or composite metal oxide material. The high mesoporosity of the materials according to the present invention allow them to be incorporated into the plates of supercapacitors. For these applications the materials should be conducting. Since capacitance varies directly with electrode area, increasing this area by incorporation of a material according to the present invention will contribute to the capacitance of the capacitor. When used in water treatment processes, beads or particles of

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the material can be dispersed in the water to facilitate removal of organics, bacteria, viruses, heavy metals and other contaminants. Alternatively the water or the liquid can be passed through a column packed with the metal oxide material. For water treatment processes it is also possible to produce magnetic metal oxide and composite metal oxide materials and utilise the magnetic nature of these materials to assist in their recovery following dispersion in the water to be treated.

Those skilled in the various arts would be able to make and utilise the materials and processes of the present invention to readily prepare materials suitable for the desired end application.

The present invention is further described with reference to the following non-limiting examples.

15 Example 1

Preparation of mesoporous iron oxide

5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 60 ml of Milli-Q water in a 100 ml beaker. The pH of the resultant solution was increased rapidly from approximately 1.4 to 8.2 using 6 M NaOH with rigorous stirring. Following this step the concentration of soluble NaNO_3 was measured to be approximately 0.6M. The beaker was then placed in a hot oven uncovered at 105°C overnight (14 hours). During this state the insoluble ferric hydroxide gel network dehydrated to form ferrihydrite and goethite, with consequential reduction in pH. The following morning the beaker was removed from the oven and the dry salty disk of very dark brown/purple material that had formed was rinsed immediately with Milli-Q water. Rinsing was performed by filling the beaker with agitation, settling the solid material briefly and pouring off the supernatant. This involved the loss of a small portion of dark coloured fines which were still suspended. The rinsing process was repeated 9 times. The material was then placed in a vacuum oven at 60°C and vacuum (625 mm Hg) and dried, prior to BET, and SEM measurement. The average particle size of the mesoporous iron oxide was > 1 micron.

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Example 2**Preparation of Iron Oxide/Activated Carbon Material**

- 5 5 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 60 ml Milli-Q water in a 100 ml beaker. 5 g of BP2000 carbon was dispersed in this solution with gentle stirring. The pH of the resultant solution was increased rapidly from approximately 1.4 to 8.2 using 6 M NaOH with rigorous stirring (magnetic bead on magnetic stirrer). The beaker was placed in the preheated oven at 105°C and left overnight leaving a dried black disk in the beaker. The
- 10 dried black disk was rinsed/washed with Milli-Q water. Rinsing/washing was performed by filling the beaker with water, followed by agitation, settling the solid material briefly and pouring off the supernatant. This process resulted in the loss of a small amount of fines. The rinsing process was repeated 9 times. The material was then placed in a vacuum oven at 60°C and vacuum (625 mm Hg) and dried, prior to BET measurement.

15

Notes.

5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ forms approximately 1 gram of Fe_2O_3 , therefore the ratio of iron oxide to carbon for this material is approximately 1:5.

20

Example 4**BET and BJH measurements**

- BET surface area measurements were determined by multi-point gas adsorption using a
- 25 Micromeritics ASAP 2400 surface area analyser. Nitrogen was used as the adsorbate at -196°C. Prior to analysis, samples were vacuum degassed, at 100°C, to an ultimate vacuum of <10 Pa.

- BET surface area is derived from the gas adsorption/desorption isotherm which is a
- 30 measure of the molar quantity (or standard Volume) of gas adsorbed (or desorbed), at a

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constant temperature, as a function of pressure. The BET equation, in its linear form, can be written as:

$$\frac{P}{V_a(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_o}$$

Where P = Pressure

5 P_o = Saturation pressure of gas

V_a = Volume of gas adsorbed at pressure P

V_m = Volume of gas adsorbed at monolayer coverage

C = BET constant

- 10 A plot of $P/[V_a(P_o - P)]$ vs. P/P_o should yield a straight line with intercept $1/V_m C$ and slope $(C-1)/V_m C$. The value of V_m is obtained from a regression line plot through the data (typically between P/P_o values of 0.05 to 0.3).

The specific surface area (s) of the adsorbent is then calculated from V_m by:

15
$$s = \frac{V_m \sigma N_a}{m V_o}$$

Where:

σ = Cross-sectional area of adsorbate.

N_a = Avagadro constant

V_o = Molar volume of gas

20

BJH method is a procedure for calculating pore size distributions using the Kelvin equation and involves conceptual emptying of condensed adsorptive (Nitrogen) from the pores in a stepwise manner as the relative pressure is likewise decreased. The pores are considered filled at the arbitrary point of about 99.5% relative pressure ($P/P_o = 0.995$) and the pore size is calculated as per the reference

25

The materials prepared in Examples 1 and 2 were subjected to BET and BJH measurements described above. The results are shown below in Table 1:

- 15 -

Table 1

	Iron Oxide*	BP2000/Iron Oxide composite	BP2000
BET Surface Area (m ² /g)	265.2 299.1 336.1	1200	1511
BJH (pore area 2-50nm) (m ² /g)	125.6 219.8 237.0	951	1150
BJH (pore volume) (cc/g)	0.0892 0.180 0.174	0.480	0.528

BP2000 is a conducting activated carbon (Black Pearls).

- 5 BET surface area is total surface area including micropores (pores < 2nm).
 BJH (pore area) is the surface area of mesopores (2-50nm diameter) only.
 BJH (pore volume) is the total volume of the mesopores (2-50nm diameter).
 *These results correspond to three different preparations following the methodology of
 Example 1.

10

Example 4

Removal of Natural Organic Matter (Humic Substances) From Water by Mesoporous Materials

- 15 A solution of Armadale fulvic acid (Contech, Canada) was prepared from a concentrated aqueous solution by dilution in the ratio 1:50 of milli-Q water and resulted in a yellow/brown solution.
 Equal portions of the dilute solution were measured into a series of four vials labelled 1 to 4. Vial number 1 was designated the blank and received no further additives. Using a
 20 spatula, approximately equal measures of BP2000 carbon, mesoporous iron (as prepared in Example 1) and carbon/iron oxide composite (as prepared in Example 2) were individually added to vials 2, 3 and 4 respectively. The vials were left overnight to equilibrate.

Observations following day:

Vial 1 – Blank, no additive – yellowish brown solution, no change

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Vial 2 – BP2000 carbon – large reduction in colour, still slight tinge of brown. Carbon was also found to float and attach to the walls of the tube, a feature which is undesirable from a separation perspective.

Vial 3 – mesoporous iron oxide – large reduction in colour although not as good as vial 2.

- 5 Vial 4 – carbon/iron oxide composite – complete removal of all colour, better performance than either vial 2 or vial 3. In addition, this material settled well in the bottom of the vial, suggesting improved properties with respect to separation, when compared with vial 2.

- 10 This experiment was also performed with a 1:10 dilution resulting in a higher concentration of NOM. The observations follow a similar pattern to above.

Observations:

Vial 1 - Blank, no additive – dark brown solution, no change

Vial 2 - BP2000 carbon – large reduction in colour (>80%), still slight tinge of brown.

- 15 Again, carbon attached to upper walls of vial and floating

Vial 3 – mesoporous iron oxide – some reduction in colour, again not as significant as in vial 2.

Vial 4 – carbon/iron oxide composite – Extremely good colour removal with only a slight tinge of brown left and much better performance than either vial 2 or vial 3.

- 20 Again, this material separates well from the solution.

The removal of colour by these additives shows the ability of the adsorbents to remove natural organic material (NOM) (a contaminant often found in waterways), from water.

This simple experiment shows the improved ability of the carbon/iron oxide composite to adsorb natural organic species over either the carbon or the iron oxide alone. Other

- 25 advantages of the composite over BP2000 are the improved surface chemical properties as evidenced by the significantly greater amount of BP2000 stuck to the upper part of the vials in both series of experiments compared to the much lesser amounts for the carbon/iron oxide composite.

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Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also
5 includes all of the steps, features, compositions, structures and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

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BIBLIOGRAPHY

E.P. Barrett et al. J. Amer. Chem. Soc. 73, p373 (1951).

- 5 Brunauer, S.; Emmett, P. H.; and Teller, E., *J. Am. Chem. Soc.* **60**, 309 (1938).

Oliviera, Luiz C. A.; Rios, Rachel V. R. A.; Fabris, Jose D.; Garg, V.; Sapag, Karam; Lago, Rochel M. *Carbon* **40**:2177-2183, 2002.

- 10 Perez-Maqueda, Luis A.; Criado, Jose Manuel; Real, Concepcion; Balek, Vladimir; Subrt, Jan. *Journal of the European Ceramic Society*, **23**:2277-2281 (2002).

Ross and Olivier, J.R, *Physical Adsorption*, J. Wiley and Sons, New York (1964).

- 15 S.J. Gregg and K. Sing; *Adsorption, Surface Area and Porosity*, Academic Press (1982).

S. Lowell and J.E. Shields; *Powder Surface Area and Porosity*, Chapman and Hall (1991)

- Schwickardi, Manfred; Jaohann, Thorsten; Schmidt, Wolfgang; Schuth, Ferdi, *Chem.*
20 *Mater.* **14**:3913-3919 (2002).

Tseng, Hui-Hsin; Wey, Ming-Yen, Liang, Yu-Shen; Chen, Ke-Hao, *Carbon* **41**:1079-1085 (2003).

- 25 DATED this 6th day of November 2003

Commonwealth Scientific and Industrial Research Organisation

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Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/AU04/001523

International filing date: 05 November 2004 (05.11.2004)

Document type: Certified copy of priority document

Document details: Country/Office: AU
Number: 2003906123
Filing date: 06 November 2003 (06.11.2003)

Date of receipt at the International Bureau: 01 December 2004 (01.12.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
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